

AD-A072 727

WASHINGTON UNIV SEATTLE DEPT OF CHEMISTRY  
HIGH TEMPERATURE GAS ENERGY TRANSFER.(U)  
AUG 79 B S RABINOVITCH

F/G 7/4

N00014-75-C-0690

UNCLASSIFIED

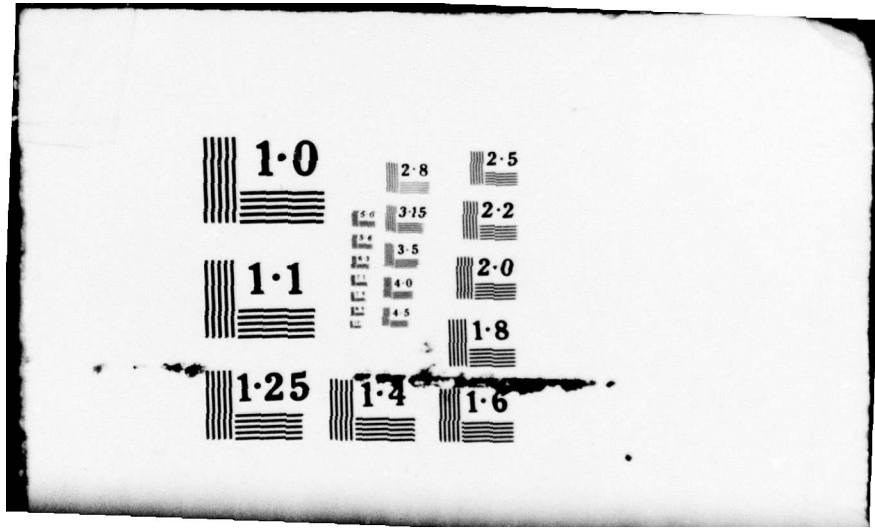
NL

1 OF 1  
AD  
A072727



END  
DATE  
FILMED

9 - 79  
DDC



A072727

DDC FILE COPY

12  
B.S.

ANNUAL SUMMARY REPORT, 1 August 1978 - 31 July 1979

High Temperature Gas Energy Transfer

B. S. Rabinovitch, Principal Investigator  
Department of Chemistry BG-10  
University of Washington  
Seattle, Washington 98195

LEVEL

OFFICE OF NAVAL RESEARCH  
Contract N00014-75-C-0690  
Project NR 092-549

DDC  
RECEIVED  
AUG 28 1979  
RECEIVED  
C

This document has been approved for public release; its distribution is unlimited. Reproduction in whole or in part is permitted for any purpose of the United States Government. This research was sponsored by the Office of Naval Research.

7 August 1979

79 08 27 068

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE  |                       | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM                                  |
|--|-----------------------|--|
| 1. REPORT NUMBER   | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER  |
| 4. TITLE (and Subtitle)<br>High Temperature Gas Energy Transfer  |                       | 5. TYPE OF REPORT & PERIOD COVERED<br>Annual Summary 1 Aug 1978-31 July 1979 |
| 6. AUTHOR(s)<br>B. S. Rabinovitch  |                       | 7. CONTRACT OR GRANT NUMBER(s)<br>N00014-75-C-0690<br>NR 092 549             |
| 8. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Professor B. S. Rabinovitch<br>Department of Chemistry BG-10<br>University of Washington, Seattle, WA 98195   |                       | 9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS                   |
| 11. CONTROLLING OFFICE NAME AND ADDRESS  |                       | 12. REPORT DATE<br>15 August 79  |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)  |                       | 13. NUMBER OF PAGES  |
|  |                       | 15. SECURITY CLASS. (of this report)   |
|  |                       | 16a. DECLASSIFICATION/DOWNGRADING SCHEDULE                                   |
| 18. DISTRIBUTION STATEMENT (of this Report)<br><br>This document has been approved for public release; its distribution is unlimited.  |                       |  |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)   |                       |  |
| 18. SUPPLEMENTARY NOTES  |                       |  |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Diffusion                      Thermal System<br>Energy Transfer              Transients<br>Gases                          Vibrational Energy<br>High Temperature              Wall Activation   |                       |  |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Work under this contract is summarized. Results on collisional transfer of vibrational energy of gases and temperature dependence of transfer efficiency by the Diffusion Cloud method are described. New results by a novel and simple Variable Encounter Method for the study of vibrational energy transfer between gas molecules and a wall, at high temperatures and levels of activation, in the transient region are reported; cyclopropane and cyclobutane have been studied. |                       |  |

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102 LF 014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

# DISTRIBUTION LIST

Contractor University of Washington

NR 092-549

Contract Number N00014-75-C-0690

Date August 1, 1979

## No. Copies

Office of Naval Research  
Code 473  
Arlington, VA 22217  
Attn: Lt. Richard Miller

10

Office of Naval Research Branch Office  
1030 East Green Street  
Pasadena, CA 91106  
Attn: Dr. R. J. Marcus

1

Office of Naval Research Branch Office  
536 S. Clark Street  
Chicago, IL 60605  
Attn: Dr. J. Smith

1

Defense Documentation Center  
Bldg. 5  
Cameron Station  
Alexandria, VA 22314

12

Office of Naval Research Branch Office  
495 Summer Street  
Boston, MA 02210  
Attn: Dr. L. H. Peebles

1

Office of Naval Research Resident Representative  
University of Washington  
1107 N.E. 45, Univ. Dist. Bldg., Rm 422  
Seattle, WA 98195

1

U. S. Naval Research Laboratory  
Code 2627  
Washington, D.C. 20375

6

Naval Research Laboratory  
Code 6100  
Washington, D.C. 20375

Naval Air Systems Command  
Code 440  
Washington, D.C. 20360  
Attn: Dr. H. Rosenwasser

1

1

|                    |  |
|--------------------|--|
| Accession For      |  |
| NTIS GRA&I         | <input checked="checked" type="checkbox"/> |
| DDC TAB            | <input type="checkbox"/>                   |
| Unannounced        | <input type="checkbox"/>                   |
| Justification      |  |
| By _____           |  |
| Distribution/      |  |
| Availability Codes |  |
| Dist               | Avail and/or special                       |
| A                  |  |



|  | <u>No. Copies</u> |
|--|-------------------|
| Naval Sea Systems Command<br>SEA-0331<br>Washington, D.C. 20362<br>Attn: Mr. J. Murrin   | 1                 |
| Naval Sea Systems Command<br>SEA-0332<br>Washington, D.C. 20362<br>Attn: Dr. A. Amster   | 1                 |
| Naval Surface Weapons Center<br>Research and Technology Dept.-WR<br>Silver Spring, MD 20910                                      | 1                 |
| Naval Weapons Center<br>Research Department<br>Code 60<br>China Lake, CA 93555   | 1                 |
| Naval Weapons Center<br>Code 608<br>China Lake, CA 93555<br>Attn: Ronald L. Derr   | 3                 |
| Air Force Office of Scientific Research<br>Directorate of Aerospace Sciences<br>Bolling Air Force Base<br>Washington, D.C. 20332 | 1                 |
| Air Force Office of Scientific Research<br>Directorate of Chemical Sciences<br>Bolling Air Force Base<br>Washington, D.C. 20332  | 1                 |
| Air Force Office of Scientific Research<br>Directorate of Physics<br>Bolling Air Force Base<br>Washington, D.C. 20332            | 1                 |
| U.S. Army Research Office<br>Chemistry Division<br>P.O. Box 12211<br>Research Triangle Park, N.C. 27709                          | 1                 |
| U.S. Army Research Office<br>Physics Division<br>P.O. Box 12211<br>Research Triangle Park, N.C. 27709                            | 1                 |
| Professor S.N.B. Murthy<br>Technical Director, Project SQID<br>Purdue University<br>Lafayette, IN 47907                          | 5                 |

This report covers the period 1 August 78 - 31 July 79

**I. Complete listing of technical reports:**

1. Technical Report TR01, 7 January 1976.  
Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures  
by B. S. Rabinovitch, D. G. Keil, J. F. Burkhalter and G. B. Skinner.

In this report a theoretical analysis was given of shock tube data for high temperature gas reactions. The data were analysed to show that collisional energy transfer efficiency appears to decrease at high temperatures.

2. Technical Report TR02, 20 April 1976  
Temperature Dependence of the Arrhenius Activation Energy. High Temperature Limit by J. F. Burkhalter and B. S. Rabinovitch.

In this report a conventional approximation to the high temperature vibrational partition function is shown to be defective, and the usual high temperature expression for the Arrhenius activation is in error. The variation of the activation energy for unimolecular reactions as a function of temperature is calculated for various representative systems.

3. Technical Report TR03, 15 October 1976  
Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems  
by D. C. Tardy and B. S. Rabinovitch.

This report gives a comprehensive and detailed survey and analysis of energy transfer in thermal gaseous systems. The present status of the field is delineated and future areas of work indicated.

4. Technical Report TR04, 15 April 1977  
On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations by S. E. Stein and B. S. Rabinovitch

This report describes an algorithm for accurate state sum and density calculations and refutes an error in the literature.

5. Technical Report TR05, 15 August 1977  
Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems by I. Oref and B. S. Rabinovitch.

In this report a simple theoretical model describing energy transfer probabilities is given. Conservation of angular momentum was imposed. The importance of completeness and detailed balance conditions and correction of an earlier model in the literature are illustrated. The model is applied to experimental data.

6. Technical Report TR06, 1 September 1977  
Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method by D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch.

A theoretical and experimental study was made of flow and diffusion of a reactant in a low pressure gas stream. Connection is made with earlier theoretical analysis.

The following were submitted in the period covered by the present report:

7. Technical Report TR07, 10 October 1978  
Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically?  
by I. Oref and B. S. Rabinovitch.

The literature is surveyed and analysed. A variety of excitation techniques including crossed molecular beam, laser, chemical activation, photochemical and thermal are considered. The answer to the title question is "yes." The relationship to the present work on intermolecular transfer is the following: multiphoton laser experiments frequently involve collisional heating of the gas. In order to understand the results, one must have a good basis for interpretation of data. In this survey, some suggested models for energy relaxation by molecular collisions are criticized and data reinterpreted in light of results obtained in this laboratory.

8. Technical Report TR08, 1 November 1978  
Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane. by E. Kamaratos, J. D. Burkhalter, D. G. Keil and B. S. Rabinovitch

A study of vibrational energy transfer by the Diffusion Cloud Method has been made at temperatures from 975 K to 1175 K in the cyclopropane isomerization system.  $H_2$ , He,  $N_2$  and  $CO_2$  were studied as inert bath gases. Their relative efficiencies increase in that order. Values of  $\langle \Delta E \rangle$  vary from  $150 \text{ cm}^{-1}$  to  $1100 \text{ cm}^{-1}$  at 975 K. It was shown that these values decline, and the collisional efficiencies,  $\beta_c$ , decrease markedly with rise of temperature to 1175 K. This is only the second measurement of such a phenomenon.

9. Technical Report TR09, 15 March 1979  
Collisional Relaxation of Non-Equilibrium Vibrational Energy Distributions in a Thermal Unimolecular System. Surface Collisions. by D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch

A novel, simple technique, the Variable Encounter Method, is described for obtaining information on energy transfer efficiency between a gas and a solid



in the transient region, and as a function of temperature. The method is as powerful as it is simple. Results for cyclopropane are described. Decrease in collisional efficiency  $\langle \Delta E \rangle$  with rise of temperature is confirmed, and the form of the transfer probability matrix  $P$  is discovered. This method and these results are considered to be some of the most innovative and important that have ever been made in this field.

10. Technical Report TR10. 15 June 1979

Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by VEM. by M. C. Flowers, D. F. Kelley, F. C. Wolters, and B. S. Rabinovitch.

Extension of the VEM technique to cyclobutane is described. An exponential form of  $P$  is required to fit the data. The value of  $\langle \Delta E \rangle$  declines with rise of temperature.

11. Listing of publications.

1. Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures, Proceed. Tenth Internat. Shock Tube Sympos. ed. G. Kamimoto, Kyoto, 1976.
2. Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems. D. C. Tardy and B. S. Rabinovitch, Chem. Revs., 77, 369 (1977).
3. On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations by S. E. Stein and B. S. Rabinovitch, Chem. Phys. Lett., 49, 183 (1977).
4. Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems, I. Oref and B. S. Rabinovitch, Chem. Phys., 26, 385 (1977).
5. Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method, D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch, J. Phys. Chem., 82, 355 (1978).
6. Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane, E. Kamaratos, J. F. Burkhalter, D. G. Keil and B. S. Rabinovitch, J. Phys. Chem., 83, 984 (1979).
7. Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically? I. Oref and B. S. Rabinovitch, Accts. Chem. Res., 12, 166 (1979).
8. Collisional Relaxation of Non-equilibrium Vibrational Energy Distributions in a Thermal System. Surface Collisions, D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, J. Chem. Phys., 71, xxx (1979).
9. Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by Variable Encounter Method. M. C. Flowers, B. D. Barton, F. C. Wolters and B. S. Rabinovitch. Am. Soc. Mass. Spectrom. Proceedings, in press.

### III. Current Work

The following work has been completed, but not reported, or is in progress.

#### 1. Diffusion Cloud Method

Experiments have been completed at 975K with inert bath gases He and N<sub>2</sub> in the two-channel 1,1-cyclopropane-d<sub>2</sub> isomerization system. In this case, information on energy transfer is obtained both from the absolute rate of isomerization to propylene — as in the c-C<sub>3</sub>H<sub>5</sub> system reported already (TR08) — but independent measurements of the energy transfer amounts  $\langle \Delta E \rangle$  to the bath gas is also deduced by deconvolution of the isotopic ratio,  $k_D/k_H$ . The values so obtained are in general agreement with each other and with the values reported earlier.

Work is continuing at high temperatures.

The theoretical analysis of reaction in laminar flow diffusion systems is also continuing. Some progress has been made. This work has been carried on by John Burkhalter.

#### 2. Variable Encounter Method

Cyclopropane: a) In addition to the work reported in TR09, additional measurements have been made on cyclopropane-d<sub>2</sub> by David Kelley on this system at two temperatures in an  $m = 3$  reactor. The work in this reactor is now complete. A report is in preparation.

b) In another apparatus, Barrie Barton has made measurements on c-C<sub>3</sub>H<sub>6</sub> in three different reactors, the results are in general agreement with the experiments of Kelley, giving slightly higher  $\langle \Delta E \rangle$  values. A report is in preparation.

c) In the same apparatus as Barton, Fred Wolters and Dr. Michael Flowers have repeated Barton's pioneering work very carefully. They obtain agreement with Kelley, but on the low side. However, all the results are considered as very satisfactory confirmation of the general reproducibility of data. A report is in preparation.

These results show that a step ladder, or narrow gaussian, is not an appropriate model for the collisional transition distribution function, and that a poisson or "linear" exponential is best.

Additional theoretical analysis of VEM systems has been made and an "incubation" time is shown to be definable in terms of the fundamental quantity, the mean first passage time.

Cyclobutane. Analysis of the data reported in TR10 has continued. The down step sizes are smaller than for cyclopropane — a very interesting finding — and an exponential model fits the transition distribution well. A complete report is in preparation.

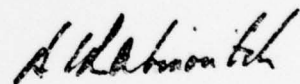
Cyclobutene. Work has started on this system which is characterized by a much smaller critical threshold than cyclobutane ( $\sim 32$  kcal vs 62 kcal).

Methylcyclopropane. Work will start soon on this species to discover the effect of variation of molecular properties on energy transfer efficiency relative to  $c\text{-C}_3\text{H}_5$  and  $c\text{-C}_4\text{H}_8$ .

#### IV. Personnel

The following graduate students and fellows have been involved on this project in the period.

Barrie Barton  
John Burkhalter  
Dr. M. C. Flowers (Senior Lecturer, Southampton University, on leave)  
David Kelley  
Dr. Efsthios Kamaratos  
Fred C. Wolters  
Dr. Lajos Zalotai (Visiting Assist. Professor from Zeged, Hungary on U. N. Fellowship)



B. S. Rabinovitch  
Principal Investigator